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14. ABSTRACT

This Final Report is in memory of the PI: Professor Ronald Eby who passed away in Sep 2006. The goal of his program was to provide the basis for membranes and coatings that will absorb strong IR radiation to protect DOD sensors. Their approach is to use the Green Fluorescent Protein (GFP) to provide the absorption and silk protein to provide a good compatible matrix. They have previously demonstrated that GFP molecules can be incorporated into cast membranes of silk from B. mori in sufficient concentration to maintain their nonlinear (strong) absorption properties. The membranes resisted visible damage to peak fluences of 0.1-0.2 J/cm2. However, the cast membranes were somewhat inhomogeneous with respect to the GFP distribution. Therefore, they were pursuing other processing methods. At present, they were producing membranes of electrospun fibers from solutions made with liquid silk from the gland of B. mori mixed with GFP. Electrospinning is rapid and allows less separation of the GFP.

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Program Title: *Optical Limiting Silk Membranes & Coatings*

Principle Investigator: *Ronald K. Eby, The University of Akron*

Co-Principle Investigators: *Sirina Putthanarat, The University of Akron*

Project Summary:

This Final Report is in memory of the PI: Professor Ronald Eby who passed away in Sep 2006. The goal of his program was to provide the basis for membranes and coatings that will absorb strong IR radiation to protect DOD sensors. Their approach is to use the Green Fluorescent Protein (GFP) to provide the absorption and silk protein to provide a good compatible matrix. They have previously demonstrated that GFP molecules can be incorporated into cast membranes of silk from B. mori in sufficient concentration to maintain their nonlinear (strong) absorption properties. The membranes resisted visible damage to peak fluences of 0.1-0.2 J/cm^2. However, the cast membranes were somewhat inhomogeneous with respect to the GFP distribution. Therefore, they were pursuing other processing methods. At present, they were producing membranes of electrospun fibers from solutions made with liquid silk from the gland of B. mori mixed with GFP. Electrospinning is rapid and allows less separation of the GFP. Polyethylene oxide (PEO) was added to the silk/GFP solution to improve the processability. The solutions were successfully elctrospun and the morphology of the fibers was characterized using optical microscopy, and scanning electron microscopy. The resulting fibers exhibit fluorescent under the UV microscope in the reflection mode indicating incorporation of the GFP. The average fiber diameter is about 200 nm. Other characterization techniques are being applied. In collaboration with Dr. Kathryn Wahl of NRL we will determine the mechanical properties of the membranes. In collaboration with Dr. Rajesh Naik of Wright Patterson, we will examine the nonlinear (strong) absorption properties of the membranes.

Other work involves a collaborative project on the use of spider silk produced by bacteria, which is being pursued with Prof. Randy Lewis of the University of Wyoming. Further work involved the use of silk with the GFP attached via genetic engineering. Also, an 11-day workshop was held with visiting scientists from Japan to transfer aspects of the art of silkworm rearing, silk gland removal, silk removal from the gland and silk casting. It was attended by scientists from the Wright Patterson Materials Laboratory and the University of Akron, Department of Polymer Science.

PROCESSING, PROPERTIES AND MORPHOLOGY OF OPTICAL LIMITING SILK MEMBRANES

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AFOSR AGREEMENT NUMBER: F49620-03-1-0169

OBJECTIVE

No change.

STATUS OF EFFORT

Good progress has been made on making thin nanocomposite membranes (1-5 μm) of aqueous electrospun silk and GFP. The GFP molecules maintain their optical properties as evidenced by fluorescence microscopy. We are currently making two-photon absorption measurements using pulses of 775 nm wavelength and 140 fs pulse width on both these membranes and cast membranes. This work is being carried out in collaboration with Rayesh Naik and others at the Wright Patterson Materials Lab.

ACCOMPLISHMENTS/NEW FINDINGS

We have shown that GFP can be incorporated in electrospun nanofibers spun from water solution. As a result, it should be possible to make such fibers with nonlinear optical properties in the near infrared. As mentioned above, we are in the process of collaboration with the Materials Lab to determine whether the GFP molecules retain their nonlinear properties when they are within the nanofibers.

We have developed a number of collaborative arrangements. The one with the Material Lab has been mentioned above. We have also developed one with Prof. Randy Lewis of the University of Wyoming to try to develop membrane casting and electrospinning methods for his MaSp2 silk made by bacteria. Similar efforts are being pursued with another Professor at the University of Akron. The goal is to make membranes from a range of spider silks with different compositions. We are also

collaborating with the same Professor to make tensile measurements on silk nanofibers. Finally, we are collaborating with Dr. Kathryn Wahl of the NRL to determine the mechanical properties of the different silk membranes and the effect of GFP "nanoparticle" on these properties. All of these collaborations have been begun.

PERSONNEL SUPPORTED

Principal Investigator: Dr. Ronald K. Eby

Dr. Sirina Putthanarat/Dr. Sureeporn Koombhongse

PUBLICATIONS (peer reviewed)

1. Nonlinear Optical Transmission of Silk/Green Fluorescent Protein (GFP) Films, S. Putthanarat, R. K. Eby, Rajesh R. Naik, Shane B. Juhl, Mark A. Walker, Elaine Peterman, Scott Ristich, Jun Magoshi, Toshihisa Tanaka, Morley O. Stone, Barry L. Farmer, Christopher Brewer, Donald Ott, Polymer, 45 8451 (2004).
2. Electrospun *Bombyx mori* Gland Silk, S. Putthanarat, R.K. Eby, W. Kataphinan, S. Jones, R. Naik, D.H. Reneker, B.L. Farmer, Polymer, In Press, (2005).
3. Epitaxy of Folds in Polycthylene Crystals: Molecular Mechanics Investigation, K.L. Anderson, B.L. Farmer, R.K. Eby, Polymer, In Press (2005).
4. Axial Deformation of Dragline Silk of *N. Clavipes*, D.V. Mahoney, R.K. Eby, In Press Journal of Macromolecular Science, (2005).
5. Morphology of PI-PEO Block Copolymers for Lithium Batteries, C. Xue, M.B.Meador, V.A. Cubon, L. Zhu, J.J. Ge, S.Z.D. Cheng, R.K. Eby, Submitted, J. Am. Chem. Soc., (2005).

6. Molecular Evidence of a Monotropic Transition in Self-assembled Discotic Liquid Crystals, C. Xue, F. Illhan, S. Jin, S.Z.D. Cheng, M.A. Meador, M.B. Meador, R.K. Eby, Submitted, J. Am. Chem. Soc., (2005).

INTERACTIONS/TRANSITIONS

A. Participation/Presentations at Meetings, Conferences, Seminars, etc.

1. Symposium on Biomimetics, Biomaterials, and Biointerfacial Science, Invited, January 2005, "Optical Limiting Silk Membranes", R.K. Eby, Dept. of Polymer Science, The University of Akron, Akron, OH.
2. International Conference on Polymer Physics/Morphology, invited, April 7, 2005, "Aspects of the Deformation of the Dragline Silk of Nephila Clavipes, R.K. Eby, Dept. of Polymer Science, The University of Akron, Akron, OH.
3. American Physical Society (APS) meeting, March 2005, "Electrospun liquid silk from the gland of Bombyx Mori silk/ Green Fluorescent Proteins (GFP)/ poly(ethylene oxide)", S. Putthanarat, W. Kataphinan, R. K. Eby, D. H. Reneker, Dept. of Polymer Science, The University of Akron, Akron, OH, R. Naik, S. Jones, AFRL/MLBJ, B. Farmer, AFRL/MLBP.
4. University of Dayton Research Institute (UDRI), Invited, November 10, 2004, "PBO based Proton Exchange Membrane (PEM) for high temperature fuel cells", S. Putthanarat. Dept. of Polymer Science, The University of Akron, Akron, OH.
5. North American Membrane Society (NAMS 04), Contributed, June 26-30, 2004, " Rigid rod polymer based Proton Exchange Membrane (PEM) for high

temperature fuel cells", S. Putthanarat, R. K. Eby, Dept. of Polymer Science, The University of Akron, Akron, OH, D. Ofer, B. Nair, Foster Miller Inc., D. Ott, Dept. of Biology, The University of Akron, Akron, OH.

B. Consultative and Advisory Functions to Materials Lab at WPAFB

1. Transferred information on structure, properties and processing of silks to various postdocs and other scientists at ML. PI and Co-PI used ML facilities for measurements on this collaborative project.
2. Collaborating with ML on preparing cast silk/GFP nanocomposite membranes and electrospun silk/PEO/GFP nanocomposite membranes.

C. Other

1. Developing project with Prof. Randy Lewis of University of Wyoming on making silk membranes from silk produced by bacteria.
2. Developing project with Kathryn Wahl of the Naval Research Laboratory on the mechanical properties of cast silk/GFP nanocomposite membranes and electrospun silk/PEO/GFP nanocomposite membrane.
3. Developing project with another Professor at the University of Akron to make membranes from a range of spider silks with different compositions as well as to make tensile measurements on silk nanofibers.

NEW DISCOVERIES

The most significant ones are those that have been mentioned already in ACCOMPLISHMENTS/NEW FINDINGS section. The fluorescent properties of nanofibers electrospun from aqueous solution containing GFP opens the door to the possibility of making nanofibers with nonlinear optical properties. These could be used to make membranes or coatings with sufficient GFP to limit transmission and protect sensors. There have been no inventions or patent disclosures.

HONORS/AWARDS

A: During Grant Period:

- Honorary Editor of *Polymer,* 2004 (PI)
- Travel Award, The North American Membrane Society, 2004 (Co-PI)
- Member – The University of Akron Patent Society, 2004 (PI)

B: Prior to Grant Period:

- Phi Beta Kappa
- Fellow – American Physical Society, 1966
- Fellow – Acoustical Society of America, 1971
- Charter Member – Federal Senior Executive Service 1979
- Fellow – Society of Plastics Engineers, 1984
- Alexander von Humboldt Senior Prize, 1989
- Endowed Chair, The University of Akron, 1990
- International Research Award - Society of Plastics Engineers, 1993
- Fellow - North American Thermal Analysis Society, 1993

- Japanese Government Research Award, Silk 1997
- Who's Who in America, 2001-
- Member NBS/NIST Distinguished Scientists Engineers and Administrators, 2003